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Popinciuc, M.; Jonkman, H. T.; van Wees, B. J.

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Energy level alignment symmetry at Co/pentacene/Co interfaces

M. Popinciuc^{a)}

Physics of Nanodevices, Material Science Centre, University of Groningen, 9747 AG Groningen, The Netherlands

H. T. Jonkman

Molecular Electronics, Material Science Centre, University of Groningen, 9747 AG Groningen, The Netherlands

B. J. van Wees

Physics of Nanodevices, Material Science Centre, University of Groningen, 9747 AG Groningen, The Netherlands

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We have employed x-ray and ultraviolet photoemission spectroscopies (XPS and UPS) to study the energy level alignment and electronic structure at the Co/pentacene/Co interfaces. In the case of pentacene deposition on Co we found an interfacial dipole of about 1.05 eV and a hole injection barrier of 0.96 eV, whereas for the case of Co deposition on pentacene we found a similar value for the hole injection barrier and vacuum level alignment (~ 0 eV interfacial dipole), respectively. By combining XPS and UPS we were able to identify that chemical reaction occurs between pentacene and Co. The results of the deposition of the reactive Co on pentacene indicates only a small penetration depth of the metal atoms into the pentacene layer. A complete band diagram for the layered Co/pentacene/Co structure is presented in the frame of a model with interfacial dipoles. Finally, our findings are linked to spin injection experiments. © 2006 American Institute of Physics. [DOI: [10.1063/1.2369651](https://doi.org/10.1063/1.2369651)]

I. INTRODUCTION

Spin electronics—spintronics—uses the carrier spin degree of freedom to manipulate information in electronic devices. Typical device geometries for the injection/detection of spins are a sandwich or a lateral structure in which the nonmagnetic material is placed between two ferromagnetic electrodes whose magnetization can be manipulated independently, by applying an external magnetic field, for example. Such a device is known as a “spin valve” and its resistance depends on the relative orientation of the magnetization of the ferromagnetic electrodes (parallel or antiparallel). Spin valve effect in organic semiconductors was demonstrated by Dediu *et al.*¹ using sexithienyl (T_6) and Xiong *et al.*² using 8-hydroxy-quinoline aluminium (Alq_3). Organic semiconductors are believed to have long spin relaxation times due to weak spin orbit interaction. Their relatively low processing temperature, i.e., cheap fabrication, and the unlimited possibilities to tune their properties offered by chemistry make them appealing for integration into spintronic devices. In the case of using organic semiconductors (semiconductors, in general) and ferromagnetic metals for building a spin valve, the high resistivity of the semiconductor (which is spin independent) is orders of magnitude higher than that of Co (which is spin dependent) and dominates the total resistance of the device. This leads to the vanishing of the spin signal, i.e., there is no measurable difference in device resistance between the parallel and antiparallel orientations of the magnetization of the ferromagnetic electrodes. This is known as the conductivity mismatch problem³ and, in order to over-

come it, one needs to increase the spin dependent part resistance of the device. This can be offered by the natural Schottky barrier (if it exists and provided that the spins are not mixed at the interface), by the insertion of a tunnel barrier or by the use of ferromagnetic semiconductors.^{3,4} Knowledge of the interfacial electronic structure (barrier heights, chemistry) is crucial for the design and operation of organic spin valves that use the ferromagnetic metal Co as the source for spins and the organic semiconductor pentacene as transport/manipulation medium of spins. The choice of Co and pentacene comes from the fact that Co is a well known and widely used ferromagnetic metal in the community of the metal spintronic devices, whereas pentacene has a high mobility, ranging from ~ 0.1 cm²/V s in thin film field effect devices up to 35 cm²/V s for high purity single crystals.⁵ Understanding the Co/pentacene/Co interfaces is equally important for the field of organic semiconductor devices in general, not only for the particular field of organic spintronics.

In this paper we report on the energy level alignment at the Co/P (i.e., pentacene deposited on Co) and P/Co (i.e., Co deposited on pentacene) interfaces, studied by photoemission experiments. By combining x-ray and ultraviolet photoemission spectroscopy experiments (XPS and UPS) one can accurately deduced the energy level alignment and the chemistry of these interfaces. Due to the high reactivity of the Co metal chemical reaction may be expected at these interfaces. The surface sensitivity of the UPS (few monolayers) enables the sampling of the electrostatic potential within pentacene as a function of its thickness atop of a Co thin film and provides clues about the energy level alignment mechanism at the interface and far from it. Moreover, a widely used

^{a)}Electronic mail: m.popinciuc@rug.nl

spin valve geometry is a stacked one in which the transport medium for spins is sandwiched between two ferromagnetic electrodes. As the deposition of metals on the loose organic matrix may be accompanied by diffusion of the metal atoms, the resulted interface is ill defined and very different from the sharp interface in which the organic is deposited on the metal. In consequence the barrier heights at the two interfaces are different and the device I - V characteristics become asymmetric, affecting the transport.⁶⁻⁸ Therefore, it is interesting to study both interfaces and we will show that they provide complementary information on the interaction between Co and pentacene.

Our results give an interfacial dipole of about 1.05 eV and a hole injection barrier of 0.96 eV for the Co/P interface, in agreement with Ref. 9. We identify that charge transfer takes place (electrons flow from P to Co) and attribute it to hybridization of the pentacene highest occupied molecular orbital (HOMO) and Co 3d band. Far from the interface the polarization energy and band bending are responsible for the energy level position. The diffusion length of the reactive Co atoms is found to be small, mostly the first monolayer being affected. At the P/Co interface we found that vacuum levels align, i.e., interfacial dipole barrier is 0 eV, whereas the hole injection barrier is similar to that of Co/P interface, namely, 0.96 eV. Finally, a complete band diagram is extracted and is presented in the frame of a model with interfacial dipoles as found for other metal/organic interfaces.^{6,7,10,11}

The paper is organized as follows. In Sec. II we will review the photoemission spectroscopy principles and discuss the relevant aspects for our research followed by the experimental details on sample fabrication and setup used. In the subsequent sections, Secs. III and IV, we present the experimental results on the energy level alignment at Co/P and P/Co interfaces, respectively. In Sec. V we draw a full band diagram for a Co/P/Co structure and present the conclusions.

II. EXPERIMENT

A. Photoemission spectroscopy principles

In this section we will briefly review some of the aspects of the photoemission spectroscopy (PES) which we find relevant in understanding the paper. For details on PES we refer the reader to, e.g., Refs. 6 and 12–14. In a PES experiment, electrons from the occupied energy levels of the sample are excited to the vacuum by the application of photons, x-ray of 1486.6 eV, and UV of 21.22 eV in our experiments. The emitted photoelectrons are then collected and analyzed as a function of their kinetic energy (KE) by an electron spectrometer analyzer. The small escape depth of the photoelectrons (tens of angstroms, depending on their energy) gives the surface sensitivity of the PES technique. With respect to Fermi level, the photoelectrons excited in the sample have a maximum kinetic energy equal to the energy of the light used ($h\nu$). The minimum kinetic energy of the photoelectrons is 0 eV. These are (multiply) inelastically scattered photoelectrons or those with a binding energy (BE) of $h\nu$ with respect to Fermi level (FL). However, only those photoelectrons with energy higher than the work function of the sample can

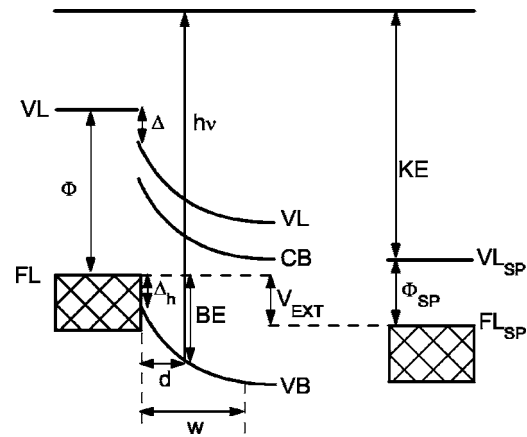


FIG. 1. Schematic of the interface formation between a metal and an organic semiconductor and the PES measurement. VL, FL, and Φ and VL_{SP}, FL_{SP}, and Φ_{SP} represent the vacuum level, the Fermi level, and the work function of the sample and spectrometer, respectively. w , Δ , and Δ_h represent the depletion width, the interfacial dipole, and the hole injection barrier, respectively.

escape to vacuum and be brought above/at the vacuum level (VL). Therefore, the difference between the light energy and the width of the measured spectrum represents just the work function (Φ) for a metallic sample or the ionization potential (IP) for a semiconducting sample. In Fig. 1 we present a schematic drawing of a PES measurement of the interface formation between a metal and semiconductor with interfacial dipole. The sample is biased negatively (V_{ext}) with respect to the spectrometer detector in order to enable the measurement of the *zero kinetic energy* electrons. These are electrons which have been excited just to the VL and are known also as the secondary cutoff electrons (SECs). The BE of the photoelectrons, with respect to Fermi level, is given by

$$BE = h\nu - KE - \Phi_{sp} + V_{ext}, \quad (1)$$

where $h\nu$ is the photon energy, KE is the measured kinetic energy of the photoelectrons, Φ_{sp} is the spectrometer work function, and V_{ext} is the applied bias. Important to note is that the binding energies of the core level electrons depend only on their chemical state and their position with respect to FL, i.e., the position of the FL in the band gap of a semiconductor. BE does not depend on the work function of the sample and therefore on any dipole present at the surface.

The work function of a metal is comprised by two contributions: the bulk chemical potential (material dependent) and the surface dipole created by the spilling out in the vacuum of the electron wave function,^{6,14} which is material and surface characteristics. Different faces of a crystal have different electronic structures of the top most atomic layers (surface to vacuum) leading to different surface dipoles and, implicitly, to different work functions. Additionally, a metal surface with a high roughness will have the surface dipoles oriented in pretty random directions which overall leads to a smaller total surface dipole. Consequently, a rough surface has smaller work function compared with a lower roughness surface. The surface dipole modification by adsorption of rare gas atoms on metal surfaces has been shown to modify (lower) the metal work function, see, for example, the case

of xenon adsorption on palladium.¹⁵ The explanation of this effect is that the electron cloud of the adsorbed Xe atoms compresses the electron cloud of the metal surface, therefore leading to a lowering of the work function of the sample. This phenomenon is generally present also at metal/organic interfaces.^{6,7} The sudden change in work function of the sample (essentially the change in the VL position with respect to FL) by the deposition of an organic material occurs mostly in the first monolayer. This is often attributed to the creation of an interfacial dipole and can have several contributions: the modification of the existent surface dipole, charge transfer due to chemical reactions, and electrochemical potential equilibration. With increasing distance from the interface (d) band bending may occur over a distance denoted w and therefore the energy levels have different positions with respect to FL as a function of d (see Fig. 1). By depositing the organic material in a stepwise manner on top of a metal and given its surface sensitivity, PES measurement allows the sampling of the energy levels alignment of the organic as a function of its thickness atop the metal substrate. Additionally, screening effects (polarization energy) and surface states (which can pin the FL) play an important role.

In this section we briefly reviewed some important aspects of the photoemission. Even though our discussion was not exhaustive, we hope that we provided the reader with the basics to understand the rest of the paper.

B. Experimental details

All experiments are carried out *in situ*, in a interconnected ultrahigh vacuum system comprising a deposition chamber (pressure of $\leq 3 \times 10^{-9}$ mbar during depositions) and an analysis chamber where the photoemission spectra are collected (base pressure of 2×10^{-10} mbar). Thin films of Co (50–100 Å) are deposited on oxidized silicon substrates by evaporation of Co from a resistively heated Radak type I cell using alumina crucible at a rate of about 1.5 Å/min. The evaporation of purified pentacene,⁹ was done from a home made pinhole source using a glass crucible. Pentacene is deposited onto the Co thin films in a sequential manner at a rate of 2.5 Å/min up to a thickness of 120 Å and 5 Å/min for higher thicknesses up to 480 Å. Pentacene was carefully degassed at about 50° below the evaporation temperature during about 12 h before the experiment. The growth rates, for both Co and pentacene, are monitored with quartz balances calibrated by atomic force microscopy or surface profilometry. For the P/Co interface we deposited Co in steps on Co/P (480 Å) substrates. All depositions are done with the substrate held at room temperature. The analysis chamber is equipped with a nonmonochromatic Al $K\alpha$ x-ray source (1486.6 eV) and a nonmonochromatic He discharge lamp (UV light of 21.22 eV). The photoelectrons were analyzed with a hemispherical analyzer for vacuum generators. The incoming light and the analyzer are at 35° with respect to the sample surface normal. The resolution was 1.5 eV for XPS and 0.15 eV and it was determined from the width of the Ag Fermi edge at room temperature (80%–20%). XPS spectra were satellite corrected. UPS spectra are recorded with a bias of –4 V applied to the sample and were not satellite cor-

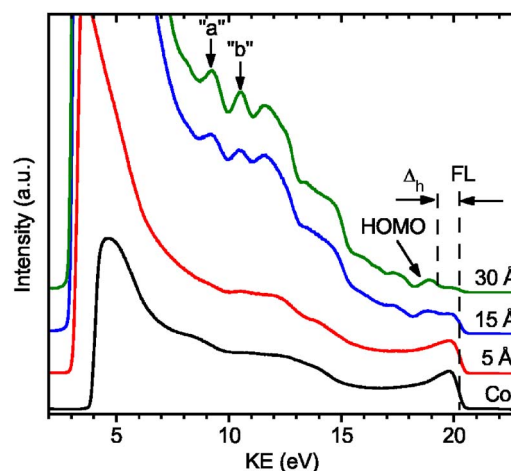


FIG. 2. (Color online) UPS spectra (KE scale) of clean Co and pentacene deposited on Co at different thicknesses of pentacene (5, 15, and 30 Å).

rected (the intensity of the 23.09 eV satellite was less than 2%). The photoemission measurements are done with the sample at room temperature immediately after each deposition step without braking the vacuum. No charging effects were observed in any of the samples.

III. CO/P INTERFACE

In Fig. 2 we present the measured UPS spectra (KE scale) as a function of the increase of the pentacene thickness deposited on Co together with the clean Co spectrum. The spectra are displaced horizontally and only a few are shown for clarity. The spectra are characterized by two sharp cut-offs. At high KE we have the FL cutoff which represents electrons excited from the FL and which are the most energetic electrons leaving the sample. At low kinetic energies we have the SEC, the onset of the photoemission, given by multiply inelastic scattered electrons generated deep in the sample. This represents the electrons excited to the VL. Subtracting the width of the spectrum from the energy of the light we get a value of 5 eV for the Co work function (spectrometer broadening corrected). The distance between leading edge of the HOMO level and FL represents the hole injection barrier Δ_h (Fig. 2). Additionally, the ionization potential (IP) of the pentacene layer is obtained in the same manner by subtracting the width of the spectrum between the leading edge of the HOMO and SEC from $h\nu$. Also, shown in Fig. 2 are some deep lying levels of pentacene, which we denoted as “a” and “b.” Later in this section we will analyze the evolution of all the energy levels with increasing pentacene nominal coverage.

After each deposition sequence an XPS spectrum was also recorded. A close-up of the SEC, HOMO, and C 1s evolution for all pentacene thicknesses investigated is shown in Figs. 3(a)–3(c), respectively. At the very first deposition step of 5 Å, we observe a sudden shift of the VL of about 0.9 eV. Up to 30 Å, that is ≈ 2 ML (monolayers) (Ref. 16) pentacene, the VL shift gradually increases and reaches a value of 1.05 eV. This shift of the VL corresponds to lowering of the work function of the sample. In the region near FL, at 5 Å pentacene the HOMO is not distinguishable but

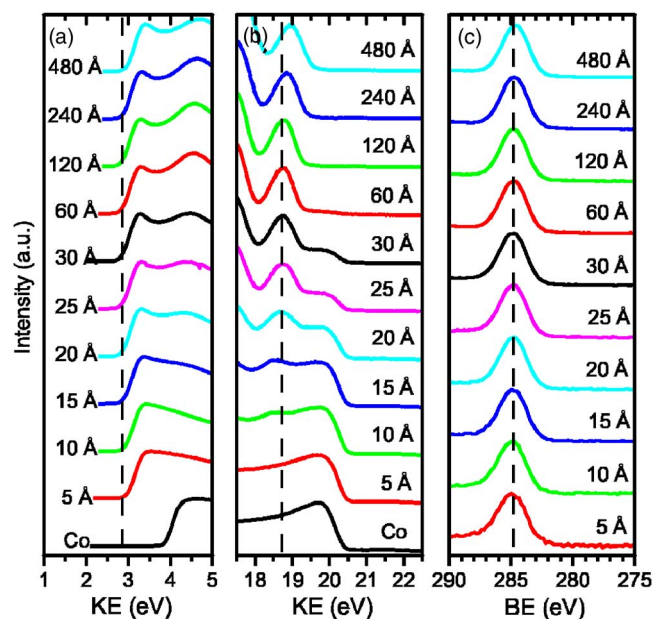


FIG. 3. (Color online) The evolution of the energy levels (normalized) with increasing pentacene thickness: a) secondary electron cutoff (SEC), b) HOMO level, and c) C 1s energy level. The vertical dashed lines represent the values of SEC, HOMO, and C 1s, respectively, at a thickness of 30 Å.

becomes visible at 10 Å [see Fig. 3(b)]. Up to 30 Å HOMO level shifts gradually to higher KE (lower BE). Estimated at 30 Å, we found a value of 0.96 eV for the hole injection barrier and 4.92 eV for the ionization potential, in reasonable agreement with previously published data.¹⁷ For pentacene coverage higher than 30 Å, VL and HOMO follow approximately the same shift towards higher kinetic energies. C 1s energy level behaves similar to VL and HOMO. This is not immediately obvious from Fig. 3(c) but it is resulting from fitting the data with a single Gaussian function after the subtraction of a Shirley type of background.¹³ The results are discussed later in this section (Fig. 5). Charging effects caused by removal of electrons from the sample can be excluded since the levels move towards lower BE, i.e., higher KE.

The position of “a,” “b,” HOMO are extracted by fitting with Gaussian functions after a linear background subtraction. Their evolution together with C 1s and VL evolution is shown in Fig. 4 as a function of pentacene coverage. The energy shifts are expressed as the binding energy shift with respect to the value at 480 Å, i.e., $BE(d) - BE(d=480 \text{ Å})$. A positive value for the energy shift of a certain energy level at a thickness of 15 Å represents a higher binding energy of the respective level for the molecules in this layer with respect to the thick layer. Note that the binding energy shift scale is flipped, so that the energy level shift resembles the schematic on Fig. 1. All energy levels follow the same trend with only slightly different shifts. The changes observed can be divided into two regimes: a *low coverage* regime for pentacene thicknesses up to 30 Å and a *high coverage* one from 30 to 480 Å. The intensity of the HOMO level and the attenuation of the spectral intensity at 19.75 eV KE (approximately at the maximum of Co 3d band position, denoted as FL intensity) saturate at a nominal thickness somewhere be-

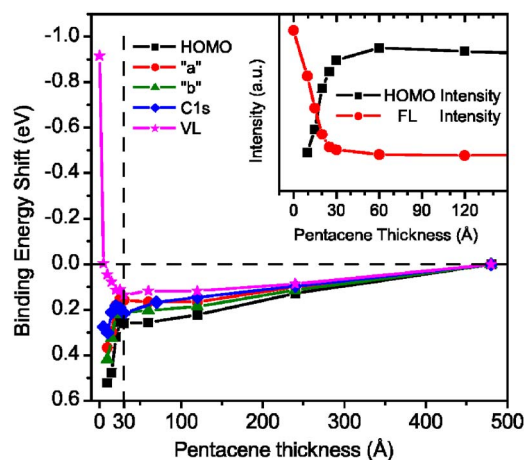


FIG. 4. (Color online) The binding energy shifts of the energy levels: HOMO, “a,” “b,” C 1s, and VL, as a function of the deposited pentacene thickness. The shifts are expressed as $BE(d) - BE(d=480 \text{ Å})$, where d represents the pentacene thickness. Note the flipped BE scale. Two distinct regimes are observed: *low coverage* up to 30 Å and *high coverage* for thicknesses higher than 30 Å.

tween 30 and 60 Å (2–4 ML) (see the inset in Fig. 4). Given the probing depth of UPS measurement of about 15 Å (1 ML), we can conclude that the growth mechanism is island type. This observation is in agreement with atomic force microscopy (AFM) measurements.⁹ Therefore, in the *low coverage* regime we are probing the *interfacial* properties whereas in the *high coverage* regime we probe the *bulklike* properties of pentacene. Next, we will separately discuss phenomena that may be responsible for the energy level alignment in the two regimes.

The low coverage regime: The interfacial energy level alignment. The vacuum level evolution gives information about the sum of all the potentials in the sample, such as interfacial dipole, charge transfer, chemical reaction, and band bending. As already pointed out, one of the widely encountered phenomenon present at metal-organic interfaces is the work function modification of the metal by the first monolayer of organic molecules, known also as the “pillow effect.”^{6,7,18–20} The electron cloud of the adsorbed pentacene molecules interacts with surface dipole of the Co substrate and compresses it, therefore the contribution of the surface dipole to the work function of Co is partly removed. This leads to the lowering of the work function and the result is an apparent interface dipole, which does not necessarily means that an interfacial dipole is created but rather that the existent surface dipole is modified. The slight bending, up to 30 Å, shows an interfacial dipole which evolves gradually. This gradual shift of the vacuum level in the low coverage regime may be explained by the following. At the initial stages of growth the pentacene molecules nucleate at step edges or defects, exactly in the regions where the surface dipole contributes less to the total surface dipole. Therefore, the interaction with the metallic substrate is apparently less than in the case of a 30 Å film situation. The random orientation of the molecules on the polycrystalline Co substrate may also lead to a smaller surface dipole. Substrate screening can play an important role as well, since the few dipoles created at the beginning of the growth will be screened by the free elec-

trons from the Co metal. These effects lead to a total measured interfacial dipole smaller than in the case when most of the molecules have the same preferred orientation.

We now turn the attention to the FL-HOMO region of the spectra in this interfacial regime. The 3d band of Co consists of orbitals which are sticking out the surface and which are very close in energy with respect to HOMO of pentacene. Such a high degree of orbital overlap may induce hybridization or chemisorption of pentacene molecules on the Co surface. Formation of new bonds or hybridization leads to the modification of the energy levels near the interface and (very) likely to charge redistribution in the interfacial layer. In the interfacial region HOMO level is found at higher binding energies compared with a thick film situation. Moreover, at a coverage of 5 Å the HOMO level is indistinguishable. These effects hint to a chemical reaction or hybridization which could lead to the formation of gap states. The high intensity at the Fermi level due to 3d band of Co hinders the clear observation of such states. In the search for the evidence of these states one may perform a multiplication of the clean Co spectrum and subtract it from the measured spectrum at 5 Å pentacene coverage. We do not perform such an operation, since the measured spectrum at 5 Å pentacene does not represent the addition of the clean Co spectrum with the 5 Å pentacene spectrum. The inelastically scattered electrons originating from the Co 3d band (at the FL) gives rise to an increase in the background at binding energies higher than of the Co 3d band and lower than that of the HOMO level. Therefore the subtraction of the Co spectrum would indicate spectral intensity in the pentacene band gap which has nothing to do with electronic states present in the band gap of pentacene. The polarization energy contribution is probably small since it is counteracted by the fact that the vacuum is not polarizable. In the case that polarization energy would dominate it would shift the energy levels towards lower binding energies, which is not the case here. It seems that hybridization gives a stronger and opposite effect to polarization energy.

Another cause for the observed high binding energy of the HOMO in the interfacial layer is the charge transfer due to chemical potential equilibration, i.e., band bending. For the purified pentacene the Fermi level sits very close to the middle of the band gap. Given the ionization potential of pentacene of 4.92 eV (see previous) it is obvious that the FL is higher in energy than the FL of Co with respect to a common VL. Therefore, FL alignment (electrochemical potential equilibration) requires then electrons to flow from pentacene to Co. This leads to a positively charged pentacene layer at the interface as compared with the situation far from the interface. The possible contribution of this effect to the observed interfacial dipole has the same sign as the pillow effect and adds up.

High coverage regime: The bulk pentacene energy level alignment. In Fig. 5 we present the C 1s energy level parameters, i.e., BE, full width at half maximum (FWHM), and intensity, extracted from fit as function of pentacene coverage. The energetic disorder (expressed by the FWHM of the C 1s line) saturates around 60 Å, before the intensity shows signs of saturation (somewhere around 120 Å). The satura-

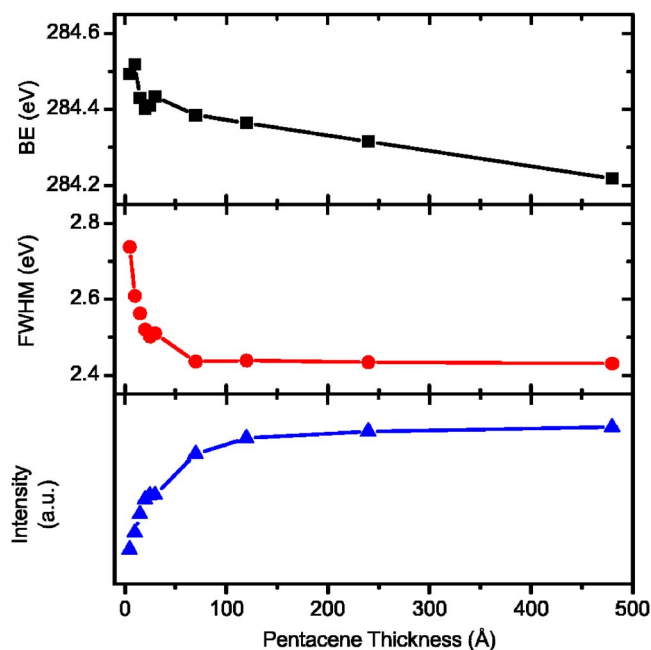


FIG. 5. (Color online) C 1s energy level parameters: binding energy (BE), full width at half maximum (FWHM), and intensity as a function of pentacene coverage.

tion in the intensity occurs when the pentacene film becomes thick enough and covers the substrate completely and starting with this thickness the interfacial layer is not probed anymore. Even though at 60 Å pentacene the intensity of the C 1s line is not actually saturated, the signal coming from the interface is negligibly small and does not have a significant contribution to the linewidth. This is consistent with the idea that the line broadening is due to different BEs for the C 1s in the interfacial layer. Turning back to UPS measurements we saw that the saturation behavior (the inset of Fig. 4) occurred at smaller thickness of the pentacene overlayer. This is expected since the kinetic energies of the photoelectrons (≈ 19 eV in UPS vs ≈ 1000 eV for C 1s in XPS) are very much different and therefore the electrons involved have different mean free paths. This results in different probing depths in the two PES experiments. We can conclude without doubt that most of the changes observed in the spectra are due to phenomena taking place at the interfacial layer. Therefore, XPS spectra at +60 Å is characteristic to the bulk properties of the pentacene film. Strictly speaking, if band bending phenomena are relevant for the energy level alignment we will probe the depletion region in this regime.

As seen in Fig. 4 the energy levels shift towards lower binding energies with increasing pentacene thickness in this *high coverage regime*. A possible cause for the monotonous shift of the energy levels is the polarization energy contribution. An increase in the polarization energy with the increase in the pentacene layer may be expected.^{10,21} This effect shifts the energy levels towards lower BE, in agreement with the behavior we observed. But, on the other hand the energy levels shift due to polarization energy contribution should show saturation behavior which is not the case for the range of thicknesses reported in this paper. We believe that the polarization energy alone cannot be responsible for these

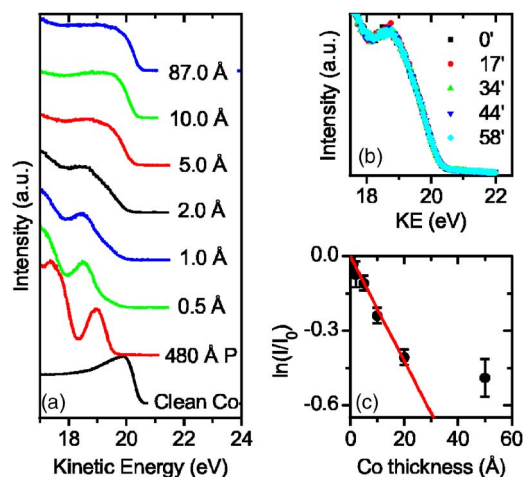


FIG. 6. (Color online) (a) UPS spectra of Co deposited on pentacene in the HOMO-FL region. Starting from the bottom: spectrum of clean Co, spectrum of 480 Å pentacene on Co, and spectra with increasing Co thickness deposited atop. The labels indicate the Co thickness. (b) The time evolution of the spectrum in the HOMO level region at 2 Å Co coverage. (c) The attenuation of the intensity of the C 1s level of pentacene as a function of the top Co layer thickness investigated in three similar samples.

shifts. As already pointed out, band bending may play an important role. In the purified, undoped, wide band gap pentacene film there are few free charge carriers available. Therefore, no significant band bending is expected for the range of thicknesses investigated. Note that we have only ~ 0.25 eV difference between the HOMO at 30 and 480 Å, and ~ 0.1 eV between VLs in the same range of thicknesses (Fig. 4). The BE of all energy levels (see Fig. 4) are higher for the interfacial layer compared with the thick film situation and all follow approximately the same shifts. This is consistent with a purely electrostatic effect and the idea that charge transfer occurs due to band bending seems to fit in this description.

IV. P/CO INTERFACE

In this section we discuss the case of Co deposition on pentacene, the P/Co. interface. Compared with the very sharp and well defined Co/P interface, the P/Co interface is more complex since metal atoms may diffuse in the pentacene layer. However, it can bring some additional information in the interaction of pentacene with Co. For example, at very low Co coverages there is no metallic surface yet, but still chemical reactions are going on. With the onset of the metallic behavior we turn on the metallic layer screening. We believe that the study of this interface brings complementary and valuable knowledge about the former well defined interface (Co/P). The experiments are done in the same manner as for the Co/P interface with the roles of Co and pentacene interchanged, that is, Co is deposited sequentially on an ~ 480 Å thin film of pentacene. We investigated this interface in three similar samples with Co as bottom metal layer (~ 50 – 100 Å). Charging effects are excluded because the Fermi edge of the top deposited Co agrees with the one of the bottom Co.

The measured UPS spectra in the region of HOMO-FL levels are shown in Fig. 6(a) as a function of Co overlayer

thickness. At a coverage as low as 0.5 Å of Co, we observe a clear shift (towards higher binding energies) and broadening of the HOMO level. We will deal later in this section with the HOMO shift. With the increase in Co layer thickness, Co 3d states arise at the FL level and start dominating the spectrum. The Fermi edge becomes clearly visible at only 10 Å Co indicating that we do not have strong diffusion of the Co atoms, probably due to high reactivity of Co atoms. However, at least the first monolayer of loose heringbone pentacene structure is mixed with Co. One may think now that the contact area between Co and pentacene is increased and the sensitivity of detecting the interfacial (band gap) states is increased. Even though it is difficult to assign the visible states between HOMO level and FL to pentacene band gap states or to Co, we believe that some of them can be attributed to hybridization between Co and pentacene energy levels.

Small penetration length and symmetric energy level alignment were reported for the case of the Ca/pentacene/Ca interface,¹¹ whereas Au and Ag showed significant diffusion and asymmetry. In Ref. 8 the authors investigated the diffusion of Ga atoms into Alq3 by tracking the Ga 3d energy levels in time at 20 Å Ga coverage. They concluded that the diffusion of Ga takes place in time whereas for the more reactive Ca this is not the case. Similarly, we monitored the spectra around the Fermi level region as a function of time at 2 Å Co coverage. The results are shown in Fig. 6(b). The spectra taken at a few intervals for 1 h do not show any changes. UPS is very surface sensitive and diffusion of the Co atoms into pentacene taking place in time would leave a clear signature in the spectra, e.g., losing some intensity around 19.5 eV. This indicates that, apart some initial intermixing, the Co atoms do not diffuse significantly in the pentacene layer. The attenuation of the C 1s level intensity with Co coverage is shown in Fig. 6(c) in an $\ln(I_d/I_{d=0})$ vs d plot, where d is the Co thickness. Up to 20 Å of Co the intensity of C 1s signal is attenuated exponentially, given by the straight line in the $\ln(I_d/I_{d=0})$ plot, consistent with a layer by layer growth of Co. Taking into account the angle of the detector with respect to sample surface normal we extract a value of ~ 58 Å for the mean free path of the photoelectrons, slightly higher than the mean free path of ~ 43 Å deduced from the attenuation of the Si 2s level of the substrate in a test sample ($\text{BE}_{\text{Si } 2s} \approx 155$ eV). These observations plus the fact that the FL is visible at only 10 Å lead to the conclusion that diffusion length of Co in the pentacene layer is small. Starting with a coverage of about 20 Å the attenuation signal deviates from the exponential behavior. We believe that this represents the clustering of the Co atoms at the very rough (due to island growth of pentacene) surface layer.

We now turn the attention to the energy level shift. At the first deposition step of 0.5 Å of Co, HOMO, C 1s, and VL shift towards higher binding energies, VL shifts in the direction of work function decrease. In fact, C 1s shift follows the shift of the HOMO level while the HOMO is still visible, therefore we use the position of C 1s to track HOMO for high Co coverage, when HOMO is not visible. As already mentioned we investigated this interface in several similar samples. In Figs. 7(a) and 7(b) we show the statistics for the

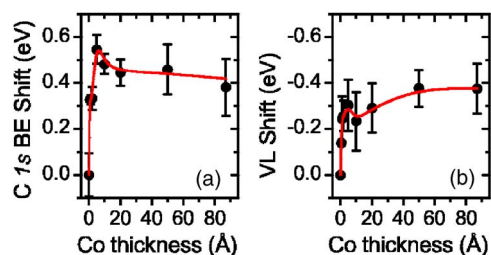


FIG. 7. (Color online) (a) C 1s energy level shift as a function of Co overlayer thickness, extracted from XPS. (b) VL (SEC) shift, extracted from UPS. Added to figure is a guide to the eyes which qualitatively represents the similar evolution of the energy levels in all the samples. Energy level shifts are expressed as $BE(d) - BE(d=0)$, where d is the thickness of the Co layer.

C 1s and VL shifts, respectively. We mention that Co energy levels (Co $2p_{1/2}$ and Co $2p_{3/2}$), as measured by XPS, do not show any significant change in BE for either of the two interfaces (not shown). Taking into account the C 1s shift of about 0.4 eV at 87 Å Co (see Fig. 7), and the position of HOMO in Fig. 4 at 480 Å pentacene we find that the BE energy of C 1s for P/Co interface is similar to that of Co/P interface. Therefore, we estimate a hole injection barrier of the same magnitude, namely, 0.96 eV. Since up to 10 Å Co we do not have a metallic behavior yet, we understand the shifting of C 1s as due hybridization and/or as the classical shift of FL through the band gap of pentacene due to high density of surface states, Co and Co-P mixed states, which appear to be enough to pin the Fermi level. As seen in Fig. 7 the C 1s shows a kinked behavior, similar to other metal (Au, Ca) on pentacene interfaces.¹¹ After 10 Å Co, which corresponds to the onset of the metallic behavior, the BE of C 1s level decreases. We attribute this behavior to the metallic layer screening, i.e., polarization energy contribution. Therefore, we conclude that at the other interface, Co/P, the C 1s energy level position contains a polarization energy contribution as well. It could not be clearly assigned due to the Co-pentacene hybridization and due to the fact that at the surface layer the polarization energy is smaller due to the fact that vacuum is not polarizable, effect which partially reduces the polarization energy.

The vacuum level shift follows qualitatively the C 1s shift. With the onset of metallic behavior (+10 Å Co) the VL shift gradually increases. We ascribe this to a developing metal surface. After 20 Å Co there are relatively small variations in the VL position. However, the values of the work function measured for the three samples differ from each other and are smaller than that of the bottom Co layer. The work function of the final surface is estimated to be about 4 eV. As already pointed out in Sec. II the work function contains a contribution from the metal surface dipole. Given the island growth of the pentacene on Co and the clustering of Co when deposited on pentacene, it is expected that the final surface of the metallic layer has a high roughness. This leads to a lower work function of the top Co with respect to bottom Co, which is in agreement with our experiments. Similar behavior was reported for Au and Ag (Ref. 11) when deposited on pentacene but it was not taken into account that the surface roughness may be responsible for such an effect.

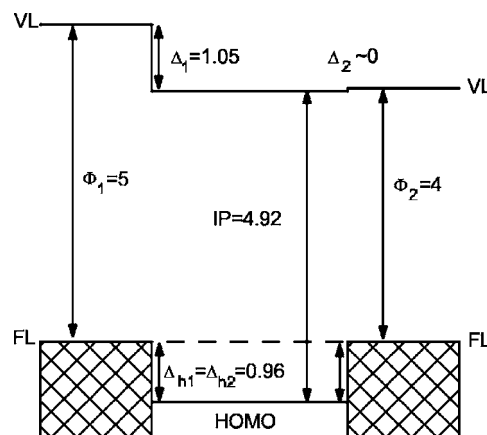


FIG. 8. Complete band diagram for a layered Co/P/Co structure. Lowest unoccupied orbital of pentacene is not included.

The magnitude of the interfacial dipole at this interface is simply the difference between VL and C 1s binding energy shifts.¹¹ This can be understood as follows. The C 1s position depends only on the position of the FL in the band gap and it is not affected by any interfacial dipole (such as P/Co dipole or Co/vacuum dipole). Since with the deposition of Co the C 1s level shifts and under the assumption of constant ionization potential of pentacene, then the VL of the buried pentacene layer must follow the same shift. Therefore, in calculating the interfacial dipole one has to take the difference between the VL and core levels shift. Using Fig. 7 we estimate a value of ~ 0 eV for the interfacial dipole at the P/Co interface, that is, the vacuum levels align at this interface. This value is much smaller compared with 1.05 eV found for Co/P interface and can be explained by the diffusion of Co atoms and the high roughness of the interface. The interfacial dipole is now a sum of individual dipoles with random orientation.

V. CONCLUSIONS

Following the discussions in Secs. III and IV we are now able to construct a band diagram for a layered Co/P/Co structure (see Fig. 8). The band diagram is drawn in the frame of a model with interfacial dipoles. The bending of pentacene bands is not included in figure since it is a small quantity and it was not clearly proven. Since the work function of the bottom and top Co layers was found to be different one may think that the Co/P/Co system can be described as a semiconductor sandwiched between two different metals. Given the IP of 4.92 eV for pentacene, a hole injection barrier of 0.96 eV, and 4 eV for the Co work function we get a value of 0.04 eV for the interfacial dipole at the P/Co interface in agreement with ~ 0 eV previously calculated.

In this paper we investigated the energy level levels alignment at Co/P/Co interfaces. At both interfaces chemical reaction (hybridization) was found. At the sharp Co/P interface we found an interfacial dipole of 1.05 eV whereas the hole injection barrier amounts to 0.96 eV. In the case of the rough P/Co interface we estimated an ~ 0 and 0.96 eV for the interfacial dipole and hole injection barrier, respectively. The hole injection barriers appear to be symmetric, an

effect which we attributed to the very small diffusion of Co atoms in the pentacene layer, due to the high reactivity of Co. This in turn supports the idea of strong chemical interaction between Co and pentacene molecules. Band bending and polarization energy effects govern the energy level alignment in the bulk and at the interfaces. The smaller value of the interfacial dipole at P/Co interface was explained by the random orientation of the individual interfacial dipoles due to island growth of pentacene. The work function of the Co top layer was found to be about 1 eV smaller than that of a smooth Co film, due to the high roughness and clustering of the Co atoms.

For spintronics applications the existence of injection barriers may allow efficient injection of spin polarized carriers in pentacene under a bias when the barrier becomes triangular and carrier tunneling from Co to pentacene is possible. The extraction of the carriers at the P/Co interface is, however, not spin dependent. In this respect, building a spin valve with clean contacts remains problematic since both interfaces have to be spin dependent.

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